## No Analytical crib available March 1, 2008 Written by Professor Cheng

No Biochemistry crib available March 1, 2008 Written by Professor Van Etten

No Physical crib available March 1, 2008 Written by Professor Raftery

## Inorganic Cumulative Exam (March 1, 2008)

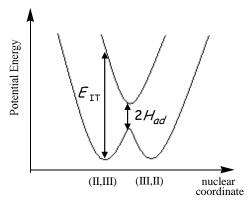
- 1 (30) A recent inorganic literature seminar was titled "Unconventional mixed valency". The following questions are about *conventional mixed valency* (stuff you may find in *Miessler and Tarr*).
  - A Sketch the structure of the Creutz-Taube ion (be as precise as you can).

$$H_3N$$
 $NH_3$ 
 $H_3N$ 
 $NH_3$ 
 $NH_3$ 

<u>B</u> Write the so-called *comproportionation* equilibrium equation for the Creutz-Taube ion

$$[Ru_{2}(II,II)]^{4+} + [Ru_{2}(III,III)]^{6+}$$
  $\sim 2 [Ru_{2}(III,II)]^{2+}$ 

<u>C</u> Provide a graphic sketch to explain the term "IVCT".



- <u>D</u> The formal oxidation potentials related to a mixed valent monocation are:  $E^{\circ}(+2/+1+) = -0.40 \text{ V}$  and  $E^{\circ}(+2/+1+) = -0.76 \text{ V}$  at 25 °C. What is the *comproportionation* constant for this mixed valent species? (2.3026 RT/F = 59.16 mV at 25 °C)  $K_c = \exp(-\Delta G^{\circ}/RT) = \exp[F(\Delta E)/RT] = 10^{6.1}$
- 2 (30) Assign symmetry point groups for the following molecules/objects (<u>mark symmetry elements clearly</u>).

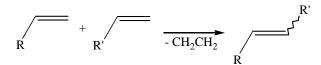
(a) $C_{2h}$	(b) $C_{\rm s}$	(c) $C_{4v}$	(d) $C_{2h}$
X	X	X X X	Y Y
(f) $D_{3h}$	(g) D <sub>2h</sub>	(h) C <sub>2v</sub>	(i) (6 pt) $T_{\rm d}$
Cl	Cl/mm.Al Al Al Cl	1	

## 3. (20) What are the SALCs made up of $\sigma$ -orbitals on F atoms that can be employed in forming P-F bonds in PF<sub>5</sub>?

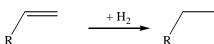
$\mathbf{D}_{3h}$	Е	2C <sub>3</sub>	3C' <sub>2</sub>	$\sigma_{\rm h}$	$2S_3$	$3\sigma_{\rm v}$	
A' <sub>1</sub>	1	1	1	1	1	1	
A'2	1	1	-1	1	1	-1	
E'	2	-1	0	2	-1	0	
A" <sub>1</sub>	1	1	1	-1	-1	-1	
A"2	1	1	-1	-1	-1	1	
E"	2	-1	0	-2	1	0	
Γ(1-3)	3	0	1	3	0	1	$= A'_1 + E'$
Γ(4,5)	2	2	0	0	0	2	$= A'_1 + A''_2$

$$F_{2} 
\downarrow P 
F_{1}
F_{5}$$

## 4 (20) Provide a representative reaction equation for reactions catalyzed by each of the following catalysts a) Grubbs $2^{nd}$ generation catalyst



b) Wilkinson's catalyst

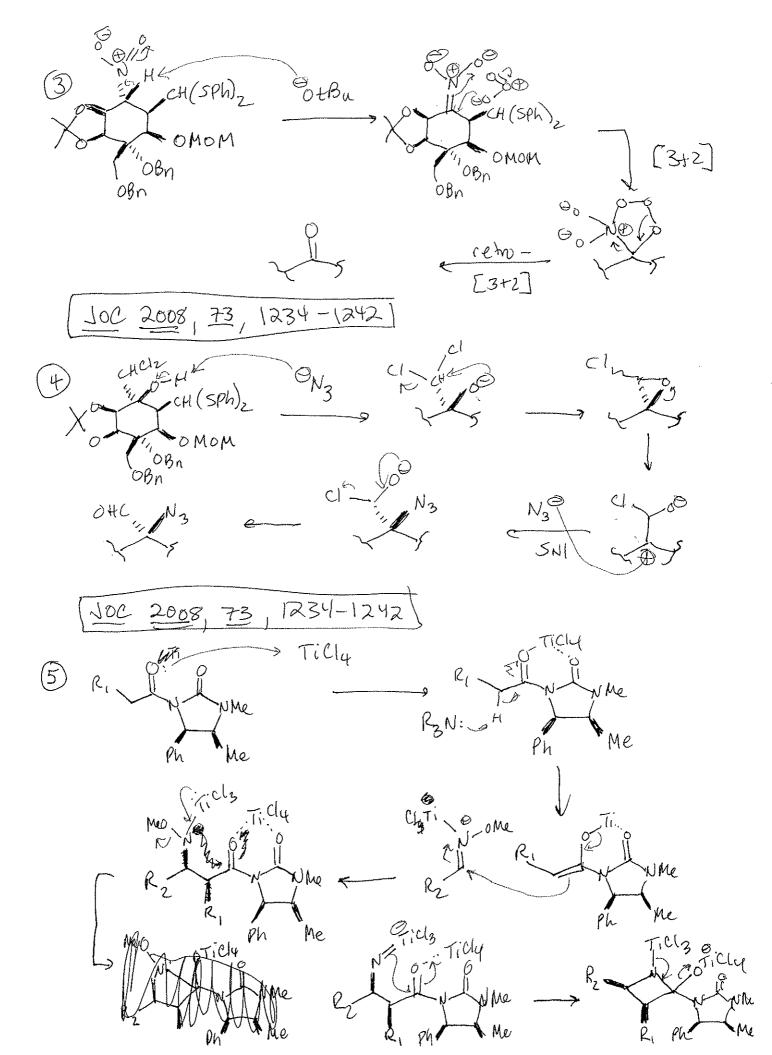


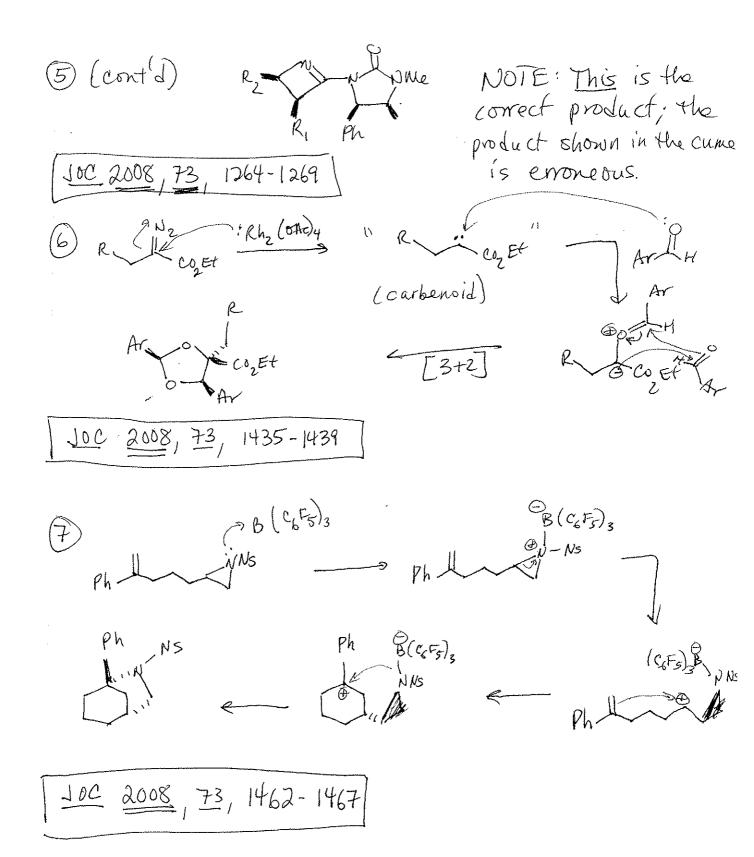
c) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>/CuI/base (Sonogashira)

$$Ar$$
— $I$  +  $\longrightarrow$   $R$   $\longrightarrow$   $Ar$   $\longrightarrow$   $R$ 

d) CuSO<sub>4</sub>/ascorbic acid (click reaction)

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